

# PATENT SPECIFICATION

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## (54) PROCESS FOR AFTERTREATING NITROGEN-CONTAINING FIBROUS MATERIALS DYED WITH REACTIVE DYES

(71) We, CIBA-GEIGY AG, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

A process for aftertreating dyeings on nitrogen-containing fibres is known from German Auslegeschrift (DAS) 1,099,494. The dyeings are obtained in acid aqueous dyebaths with soluble dyes which contain at least one mobile fibre-reactive halogen atom, and the aftertreatment is effected by raising the pH of the dyebath to above 6, in particular to 6.5 to 8.5, when the desired amount of dye has exhausted onto the fibres. This aftertreatment improves the fixation of the dye on the fibres and thereby the fastness of the dyeing.

German Auslegeschrift 2,104,348 discloses a further process for fixing dyes. Natural or synthetic polyamide fibres are dyed with reactive dyes by the exhaustion process, wherein the dyeing preparations, in addition to the reactive dye, contain an alkali donor, for example sodium trichloroacetate, which in the course of the dyeing operation effects a rise in the pH value and thereby an improved fixation of the dye. If desired, the alkali donor can be added to the dyebath only towards the end of the dyeing operation.

In both these processes, the dyed fibrous material is given an aftertreatment by rinsing and, as circumstances require, neutralising and drying them.

The fastness properties, for example the fastness to washing, perspiration, or especially the fastness to rubbing, of the fibrous material aftertreated by the known processes, are not satisfactory in every respect.

It has now been found that the fastness properties of nitrogen-containing fibrous material dyed with reactive dyes can be improved by treating the material which has been dyed in conventional manner by the exhaustion process in an acid dyebath, to which have been added in succession an inorganic or organic base, an organic acid and a reducing agent, an oxidant and optionally a fabric softener, and subsequently subjecting it to an aftertreatment by draining and drying.

The present invention therefore provides a process for aftertreating dyeings on natural, nitrogen-containing fibrous material, which have been effected in an acid dyebath with reactive azo dyes, which contain as reactive groups radicals of a carboxylic acid which contains at least one reactive halogen atom and/or a multiple carbon-to-carbon bond that is capable of addition to the nitrogen-containing fibrous material, vinylsulphone groups or groups that form vinylsulphone groups under the dyeing conditions, or the radical of an aromatic nitrogen heterocyclic ring system with two ring hetero atoms and at least one reactive halogen atom, which process comprises treating the dyed fibrous material in the exhausted aqueous dyebath in a single bath, but stepwise in succession,

- (a) at 70° to 80°C in an aqueous liquor having a pH of 8 to 9,
- (b) at 55° to 65°C with a reducing agent and a pH of 4.5 to 5.5,
- (c) at 55° to 65°C with an oxidant to remove excess reducing agent, and optionally

(d) at 30° to 40°C with a fabric softener, and subsequently finishing said fibrous material by draining and drying it.

The aftertreatment process of the present invention can be used for dyeings on any natural, nitrogen-containing fibrous material, especially on wool.

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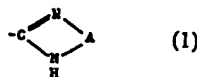
The aftertreatment process is especially advantageous for dyeings on wool which has been provided with a shrinkproof finish, since it is able to improve the fastness properties of the dyeings, so that the dyed fibrous material meets the stringent wash conditions for fibrous material, in particular wool, which has been provided with a shrinkproof finish.

When shrinkproofing wool, a distinction is made between oxidative and additive (finish with a synthetic resin) treatments, although these processes can also be combined and, where appropriate, also carried out simultaneously.

In the oxidative processes it is possible to use, for example, peroxymono-sulphuric acid, potassium permanganate, chlorine or compounds which split off chlorine, for example dichloro- and trichloroisocyanurate, normally followed by a reducing step with, for example, sodium hydrogen sulphite to remove any unreacted oxidant.

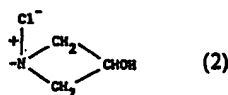
Far more important, however, are the processes in which the wool is pretreated with an oxidant, for example chlorine or a chlorine donor, and then with a synthetic resin. Examples of synthetic resins which are suitable for this combined shrinkproof finish are cationic polyelectrolytes, i.e. polymers with numerous cationically ionisable sites, for example amine or amide groups.

Thus US patent 3,300,406 discloses polymers with a main chain consisting exclusively of carbon atoms and to which the units of formula



are attached, wherein A represents alkylene of 2 to 3 carbon atoms. Such polymers can be obtained by reacting a diamine or polyamine with a polymer of a monomer which contains nitrile groups (acrylonitrile). A particularly preferred polymer is, for example, a polyvinyl imidazoline.

Another polymer which can be used for the shrinkproof finish is a polyamide of adipic acid and diethylenetriamine which is partially crosslinked with epichlorohydrin (British patent 865,727). The essential cationic functional groups in the polymer are azetidinium chloride groups of the formula



Further polymers suitable for the combined shrinkproof finish are, for example, polyvinyl pyridines, polypropylenepolyamines, polyacrylic amides, which can be methylolated, polyamide/epoxide reaction products or mixtures of polyamides and epoxides. The epoxides can be bisphenol A/epichlorohydrin resins, whereas the polyamides can be obtained from fatty acids and polyalkylene polyamines.

Shrinkproof finishes on wool without an oxidative pretreatment can also be obtained with reactive polyolefins, certain polyurethanes, reaction products of epoxides with fatty amines and dicarboxylic acids or polyamides and especially with polymers which contain thiol terminal groups. These polymers which contain thiol terminal groups (polymercaptans) are, for example, reaction products of polyalcohols, alkylene oxides with thioacids as disclosed in US patent 3,645,781. Optionally, these polymercaptans can also be applied together with other, in particular nitrogen-containing, condensation products, for example polyamide/epichlorohydrin resins. The shrinkproof finish is carried out by known methods, chiefly by padding the wool with aqueous solutions or emulsions of the cited polymers at 10° to 50°C, preferably at room temperature. The wool can be in the form of piece goods, i.e. wovens and knits, and, in the processes in which oxidants are used, also in other states of processing, for example loose wool, slubbing or yarn.

Suitable reactive dyes for dyeing the nitrogen-containing, natural fibrous material are advantageously anionic water-soluble dyes. Preferred dyes are those whose anionic character is determined by metal complex formation alone and/or by acid salt-forming substituents. Examples of such acid groups are carboxylic acid groups, acid sulphuric acid and phosphoric acid ester groups, phosphoric acid

groups, acylated sulphonamide groups, such as alkyl- or arylsulphimide and alkyl- or arylcarbonylsulphimide groups, and, above all, sulphonic acid groups. Particularly good results are obtained in general with dyes which contain at least one sulphonic acid group.

The reactive dyes are especially anionic azo dyes. These last mentioned dyes can be metal-free, metallisable or heavy metalliferous monoazo, bisazo and polyazo dyes.

The reactive azo dyes can contain, for example, the following reactive groupings: the radical of an acid which contains at least one reactive halogen atom and/or a multiple carbon-to-carbon bond which is capable of addition to this nitrogen-containing porous material, for example of chloroacetic or bromoacetic acid,  $\beta$ -chloropropionic and  $\beta$ -bromopropionic acid,  $\alpha,\beta$ -dibromopropionic acid, tetrahalogenocyclobutanecarboxylic acid, such as 2-chloro-2-fluoro-3,3-difluoro- or 2,2,3,3-tetrafluorocyclobutane-1-carboxylic acid, propiolic acid, acrylic acid, methacrylic acid,  $\alpha$ -chloroacrylic,  $\beta$ -chloroacrylic,  $\alpha$ -bromoacrylic and  $\beta$ -bromoacrylic acid,  $\alpha,\beta$ - and  $\beta,\beta$ -dichloroacrylic or  $\alpha,\beta$ - and  $\beta,\beta$ -dibromoacrylic acid, trichloroacrylic or tribromoacrylic acid, 2-(2,2,3,3-tetrafluorocyclobutyl-1-) acrylic acid, crotonic acid,  $\alpha$ - or  $\beta$ -chlorocrotonic or  $\alpha$ - or  $\beta$ -bromocrotonic acid,  $\alpha,\beta$ -dichlorocrotonic acid, vinylsulphonic acid,  $\beta$ -chlorovinylsulphonic acid, or a radical which, under the given dyeing conditions, is able to form a reactive vinylsulphone group, for example  $\beta$ -hydroxyalkylsulphonyl,  $\beta$ -hydroxyalkylsulphonamido or  $\beta$ -hydroxyalkylcarbonamido groups which are esterified with strong acids, such as the  $\beta$ -haloethylsulphonyl  $\beta$ -sulphatoethylsulphonyl,  $\beta$ -sulphatoethylsulphamoyl,  $\beta$ -sulphatoethyl-N-methylsulphonamide or  $\beta$ -sulphatopropionamido group; the  $\beta$ -alkyl- or  $\beta$ -phenylsulphonylalkylsulphonyl,  $\beta$ -alkyl or  $\beta$ -phenylsulphonylalkylsulphonamide or  $\beta$ -alkyl- or  $\beta$ -phenylsulphonylalkylcarbonamide group, for example the  $\beta$ -phenylsulphonylpropionamido group. Reactive dyes containing these reactive groupings, especially vinylsulphone groups or groups that form vinylsulphonyl groups, are preferred. The reactive group can also consist of the radical of an aromatic nitrogen heterocyclic ring system which advantageously contains two ring heteroatoms and preferably at least one reactive halogen atom, for example a fluorine, chlorine or bromine atom, or also an acryloyl, N-hydroxymethylene-amino, sulphonic acid or alkylsulphonyl group, attached to a ring carbon atom.

As examples of such reactive groups there may be mentioned: diaziny radicals containing at least one reactive halogen atom, for example halopyrimidine or halopyrimidinecarboxylic acid radicals. Dihalo- or trihalopyrimidyl radicals, such as the 2,4-dichloropyrimidyl or especially the 2,4,5-trichloropyrimidyl, 2,4,5-tribromopyrimidyl, 2,4,5-trifluoropyrimidyl and 5-bromo-2,4-dichloropyrimidyl radical, may be mentioned as specific examples.

Examples of further possible reactive groups are: the radical of 2,3-dihaloquinoxalinecarboxylic or 2,3-dihaloquinoxalinesulphonic acid, of 2-halo- or 2-methylsulphonylbenzothiazole- or -oxazolecarboxylic or -sulphonic acid, of 1,4-dihalo-phthalazinecarboxylic acid, of 2,4-dihaloquinazolinecarboxylic acid or 4,5-dihalo-6-pyridazon-1-yl-alkylene- or -phenylenecarboxylic acid, for example the acid radicals of 2,3-difluoro- or 2,3-dichloroquinoxaline-6-carboxylic or -6-sulphonic acid; 2-chlorobenzothiazole- or -oxazole-5- or -6-carboxylic or -5- or -6-sulphonic acid; 1,4-difluoro-, 1,4-dichloro- or 1,4-dibromophthalazine-6-carboxylic or -6-sulphonic acid; 2,4-dichloroquinazoline-6- or -7-carboxylic acid, 4,5-dichloro-6-pyridazon-1-yl-trimethylene- or 1',4'-phenylenecarboxylic acid; also trichloropyridaziny carboxylic acid, 3-chloropyridazine-6-carboxylic acid.

In addition to containing the reactive dyes, the dyebaths can contain as a rule in addition one or more non-ionogenic and/or anionic surfactants.

Examples of suitable anionic surfactants are sulphonated addition products of 1 to 10 moles of ethylene oxide and higher fatty acids, higher aliphatic alcohols and alkyl phenols whose alkyl chain contains 8 to 20 carbon atoms, also alkylsulphonates containing 10 to 20 carbon atoms in the alkyl chain, alkylbenzenesulphonates with a straight or branched alkyl chain containing 8 to 20 carbon atoms, such as nonylbenzenesulphonate, 1,3,5,7-tetramethyloctylbenzenesulphonate or octadecylbenzenesulphonate, as well as alkyl-naphthalene-sulphonates, for example bisnaphthylmethanesulphonate or sulphosuccinic acid esters, such as sodium dioctylsulphosuccinate.

Non-ionogenic surfactants are, for example, polyglycol ethers of alkylated phenols containing at least 7 carbon atoms in the carbon chain and 4 to 30 alkyleneoxy groups, also N-acylated-*p*-hydroxypropylamides of higher fatty acids

containing 10 to 20 carbon atoms, for example lauric, myristic, palmitic, stearic or oleic acid or of coconut oil fatty acid mixture, or also alkylpolyglycol ethers containing 10 to 18 carbon atoms in the alkyl chain and 5 to 20 ethyleneoxy groups, and polyglycol ethers containing basic nitrogen atoms, for example products which can be obtained by reacting 1 mole of an amine with 3 to 100 moles of an alkylene oxide, for example the reaction product of 1 mole of dodecylamine.

Further customary additives can be electrolytes, acids, bases, urea, thiourea, thiodiethylene glycol and hydrophilic compounds which are sparingly soluble in water, for example butyl or benzyl alcohol.

The amounts of the substances to be added to the dyebaths can vary within relatively wide limits. The amount of dye depends on the desired colour strength and is in general between 0.1 and 8%, referred to the weight of the fibres. The non-ionogenic or anionic surfactants as well as other assistants are generally added in amounts of 0.01 to 4 percent by weight, preferably 0.1 to 1.5 percent by weight, referred to the weight of the fibres.

The natural nitrogenous, in particular keratinous, fibrous material, and preferably wool, which is provided with a shrinkproof finish, can be dyed in known manner by the exhaustion process, the liquor ratio being advantageously from 1:10 to 1:40 and the pH of the liquor being from 2.6 to 6, preferably 4 to 6. It is advantageous to allow the dye liquor and the goods, without the dye, to circulate first for 10 to 30 minutes at 20° to 40°C. The dye is then added and the temperature of the dyebath is raised to boiling temperature in the course of 50 to 70 minutes and dyeing is performed at this temperature for 45 to 90 minutes.

The single-bath aftertreatment according to the invention of the dyed fibrous material over several steps in the almost exhausted dyebath is subsequently carried out by cooling the bath to 70° to 80°C, preferably to 80°C, and adjusting the pH of the liquor to 8 to 9, preferably 8 to 8.5, by adding an inorganic or organic base.

Examples of suitable inorganic bases which can be used are: ammonia, alkali carbonates or bicarbonates, in particular sodium and potassium carbonate or bicarbonate, or alkali ortho- or polyphosphates. Organic bases are chiefly nitrogen-containing bases, for example low molecular alkylamines or alkanolamines containing up to 4 carbon atoms in the alkyl moiety, in particular monoethanolamine, diethanolamine and triethanolamine.

After this first step of the aftertreatment process, which can last 10 to 20, preferably 15, minutes, the liquor is further cooled, for example by adding cold water. The addition of the reducing agent to the liquor, which has been adjusted to a pH of 4.5 to 5.5, preferably to 5, with an organic acid, preferably a low molecular organic acid containing 1 to 4 carbon atoms, for example formic, acetic or oxalic acid, is made at 55° to 65°C, preferably at 60°C. The purpose of the reductive treatment is in particular to destroy dye which has become detached from the fibre in the first step, i.e. non-fixed dye, in order to prevent a redeposition of this dye on the dyed material. Reducing agents which are very suitable for this purpose are in particular the alkali dithionites, in particular sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ). The reductive treatment can also last 10 to 20, preferably 15, minutes.

Excess reducing agent is removed by oxidation in a third step, wherein the goods are treated in the liquor for 10 to 20 minutes at the same temperature. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is a particularly suitable oxidant for this purpose. The amount of hydrogen peroxide is 0.5 to 1 ml (35%) per litre of liquor. The treatment time is approximately the same as that indicated for the previous steps.

The liquor is subsequently cooled to 30° to 40°C, preferably to about 40°C, and the goods are treated in a fourth — optional — step with a conventional fabric softener to improve the handle of the dyed material, where this is necessary. Here too the treatment time is 10 to 20 minutes, preferably 15 minutes, and the treatment is carried out at the indicated liquor temperature of 30° to 40°C.

Suitable fabric softeners are, for example, oil, fat and wax emulsions, fatty acid condensation products or also polyethylene, polyethylene glycol, siloxane and silicone emulsions. Optionally, mixtures of these fabric softeners can also be used.

Examples of suitable fatty acid condensation products are: fatty acid methylolamides, optionally reacted with thioglycolic acid or aminoplast precondensates, fatty acid/polyalkylene-polyamine reaction products, optionally reacted with ethylene oxide or other epoxide or epoxide reaction products, or also ammonium salts of fatty acid/polyalkylene-polyamide condensation products. The fatty acids contain 12 to 24, preferably 16 to 22 carbon atoms, and are, for example, lauric, myristic, palmitic, stearic, arachidic or behenic acid.

The fabric softeners are preferably added in emulsified form to the exhausted

liquors. The fabric softener emulsions can contain 10 to 30 percent by weight of active substance. The amount in which a 20% emulsion is applied is 0.5 to 4 percent by weight, referred to the weight of the fibrous material.

Particularly suitable, for example, are fabric softener mixtures which contain for example 50 to 80 parts by weight of a polyethylene (contains carboxyl groups) introduced by partial oxidation and 20 to 50 percent by weight of a condensation product of dimerised unsaturated fatty acids and polyalkylenepolyamines, for example diethylenetriamine and triethylenetetramine, or 50 to 80 parts by weight of the cited polyethylene, 10 to 30 parts by weight of paraffin (melting point range 50° to 75°C) and 10 to 20 parts by weight of the cited condensation product. The dimeric unsaturated fatty acids can be derived from, for example, unsaturated fatty acids containing 16 to 22 carbon atoms; preferably linoleic, linolenic, elaeostearic or clupadonic acid is used.

After this single bath, multistep aftertreatment the fibrous material is drained and dried. As a modification of the aftertreatment process described herein, an aqueous rinsing bath to rinse the fibrous material at room temperature can optionally be used after the treatment in the alkaline liquor (step a). The aftertreatment is then continued in warm liquor (about 60°C) in accordance with steps b) to d). By means of this rinsing process it is possible to improve the end-use properties (fastness to rubbing, perspiration and washing) of wool dyeings on material which has not been pretreated, i.e. not provided with a shrinkproof finish. Dyeings are obtained with very good wetfastness properties and markedly better fastness to rubbing in comparison to dyeings which have only been subjected to the conventional aftertreatment with ammonia.

Another advantage of the process of the present invention lies in the saving of water by carrying out the process in a single bath and not having to use a new finishing liquor for each treatment step. In addition, the process is substantially shortened, since a subsequent rinsing procedure is no longer necessary, thereby also at the same time saving much water and producing correspondingly less effluent. The amount of water necessary for rinsing is about two to four times the amount of water which is used in the dyeing and aftertreatment bath. The amount of effluent can be substantially reduced with the process of the present invention.

There follow hereinafter firstly instructions for the shrinkproof finishes and the dyeing procedure, then follow the working examples for the aftertreatment process of the present invention. The parts and percentages are by weight.

#### Shrinkproof Finish

A. A 50 cm wide horizontal paddler is so adjusted that it is able to process 20 slubbing strips with an average weight of 20 g/m and runs at a speed of 5 m/min, whereby a 120% pick-up of solution, referred to the weight of the slubbing, is obtained.

Two solutions are prepared as described hereinbelow, the percentages being by weight.

#### Solution 1

5% of sodium dichloroisocyanurate

1% of polyethyleneoxy alkylphenol

0.7% of morpholine (stabiliser)

temperature = 20°C

pH = 6.3

#### Solution 2

1% of sulphuric acid

0.8% of polyvinylimidazoline

temperature = 20°C

pH = 1.6

The solutions (1) and (2) are mixed in the volume ratio of 1:1 and added to the padding liquor (pH = 2.4). During the process, the padding liquor is kept at a constant volume by the continuous addition of further amounts of solutions (1) and (2). After it has been padded, the slubbing is left to lie for 10 minutes in a drainer cage before being conveyed to a backwashing machine for the further treatment in the following solutions:

a) aqueous rinsing bath of 20°C

b) solution containing 4% of sodium sulphite, 1% of sodium bisulphite, pH 7.6, 25°C. This bath is kept at a constant strength by adding 15% sodium sulphite solution.

c) aqueous rinsing bath.

The slubbing is then dried.

The slubbing was spun and knitted to a piece with a good shrinkproof finish.

B. A wollen fabric (100%) is impregnated at room temperature with the following aqueous liquor:

90 parts of polythiol A (40% aqueous emulsion)

12 parts of condensation product I (20% aqueous solution)

2 parts of the adduct of 9 moles of ethylene oxide and 1 mole of p-tert.-nonylphenol (75% aqueous solution)

20 parts of sodium carbonate

876 parts of water

1000 parts

The fabric is padded and squeezed out to 80% liquor pick-up. It is subsequently dried for 2 to 4 minutes at 110° to 130°C.

#### Polythiol A

A mixture of 800 g (0.2 g/mole) of a thiol with an average molecular weight of 4000, obtained from glycerol and propylene oxide, 55.2 g (0.6 g/mole) of thioglycolic acid, 5 g of toluene-p-sulphonic acid and 350 ml of toluene is heated to reflux, with stirring, in a nitrogen atmosphere. The water which has formed during the reaction (10.8 ml, 0.6 g/mole) is removed as an azeotrope with toluene. The mixture is cooled and washed with water and the organic layer is separated. The solvent is then removed from the organic layer in vacuo to leave as residue 793 g (theoretical yield = 94%) of the desired tris-(thioglycolate) with a thiol content of 0.59 equivalent/kg.

The emulsions containing the polythiol are prepared by dissolving 0.5 part of sodium carboxymethyl cellulose in 44.5 parts of water at 70° to 80°C, allowing the solution to cool, adding 50 parts of the polythiol and 5 parts of a wetting agent (adduct of p-nonylphenol and 9 moles of ethylene oxide), and stirring for 5 minutes in a high-speed mixer.

#### Condensation Product I

3 moles of diethylenetriamine are heated firstly with 1 mole of dicyandiamide and then with 2 moles of dimethyl adipate. This reaction product is then heated with 4.5 moles of epichlorohydrin and the resin is subsequently diluted with water, so that a 20% solution of condensation product I is obtained.

C. Wool slubbing is pretreated in a sulphuric acid aqueous liquor (pH 2) with sodium hydrochlorite in such an amount that 1% of chlorine is present on the wool fibres.

The chlorinated wool is then treated with a solution of 6 g/l of sodium bisulphite and then with a solution of 9 g/l of sodium hydrogen carbonate, and immediately afterwards thoroughly rinsed in cold water and dried.

The wool is afterwards padded with 8.5 g/l of a 10% aqueous solution of a polyamide/epichlorohydrin resin (obtained from adipic acid, diethylenetriamine and epichlorohydrin) and squeezed out to a pick-up of 100%, then dried for 10 minutes at 85°C and cured and finally aftertreated by rinsing and drying.

#### Dyeing Procedure

D. Finished knitted material or yarn of undyed wool, which has been provided as slubbing with a shrinkproof finish (method A or C), or correspondingly finished woollen fabric (method B), is dyed in an aqueous liquor (liquor ratio 1:35 to 1:40) as follows:

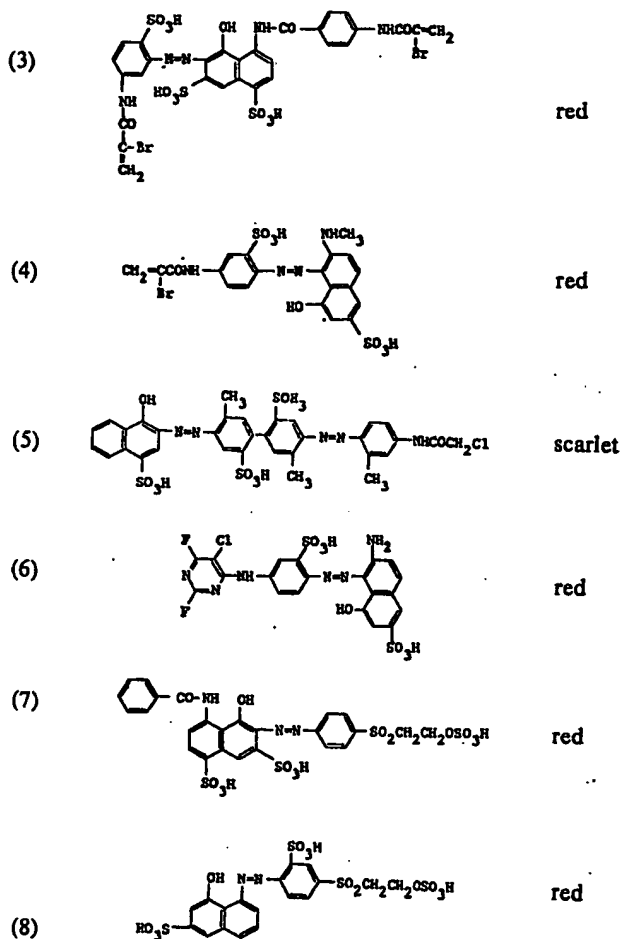
2% of ammonium sulphate

1% of a reaction product of 1 mole of a fatty amine and 7 moles of ethylene oxide, quaternised with chloroacetamide (54% aqueous solution)

1% of the ammonium salt of the acid sulphuric acid ester of the reaction product of 1 mole of a fatty amine and 7 moles of ethylene oxide (54% aqueous solution) and

acetic acid (80%), to adjust to pH to 4.5 to 5, are added to the liquor at 20°C. The liquor and the goods are allowed to circulate for 15 minutes at 20°C, then X% of a reactive dye is added, the liquor is heated to 70°C in 50 minutes and kept thereat for 15 minutes. The liquor is then heated to boiling temperature (98°C) in 30 minutes and dyeing is performed for 90 minutes at this temperature. The percentages refer to the weight of the material.

Dyes of the following formulae can be used in the dyebaths:



#### Example 1.

Woollen serge which has been given a shrinkproof finish according to method B is dyed with

a) 4.5% of the dye of formula (3)

b) 4% of the dye of formula (6)

c) 5% of the dye of formula (7)

by the exhaustion process (dyeing procedure D) and subsequently aftertreated in the almost exhausted dyebath as follows:

a) cooling the liquor to 80°C addition of 8% of ammonia (24%), pH of the liquor 8.5, duration of treatment: 15 minutes.

b) cooling the liquor to 60°C by running in cold water, adjusting the pH to 5 by adding 80% acetic acid. After about 5 minutes, 0.25% of sodium dithionite mixed with sodium pyrophosphate is added to the liquor. Duration of treatment: 10 minutes.

c) Addition of 1 ml/l of H<sub>2</sub>O<sub>2</sub>. Duration of treatment: 10 minutes. Afterwards cooling the liquor to 40°C by running in cold water.

d) Addition of 2% of an aqueous polyethylene emulsion (25%) (fabric softener). Duration of treatment: 15 minutes at 40°C.

The wool is subsequently drained and dried.

The following fastness properties are tested:

- perspiration, alkaline — SNV 195824/1961. The change in shade and the staining of wool (wool shrinkproofed according to method C) and cotton are determined. Rating in each case from 1 to 5.
- 5 — Washfastness — IWS TM 193 (American Dyestuff Reporter 35 (1973)). Determination of the change in shade and of staining as in the determination of the fastness to perspiration.
- Fastness to rubbing — SNV 195831
- Rating 1 to 5 (maximum rating = 5).

TABLE 1

dyed with dye	perspiration alkaline			washfastness			fastness to rubbing	
	change in shade	staining		change in shade	staining		dry	wet
		wool	cotton		wool	cotton		
formula (5)	5	5	5	4-5	5	5	4	4
(6)	4-5	5	4-5	4-5	5	4	4	4
(7)	4-5	4	4	3-4	5	5	4	4

The results of Table 1 show that very good general fastness properties can be obtained.

The shrinkproof finish is not adversely affected by the aftertreatment.

Example 2.

- 15 The wool in the form of hanks (shrinkproofed according to method A) which is dyed by dyeing procedure D with 5% of the dye of formula (3) is aftertreated as described in Example 1 and tested for the fastness properties indicated therein. For comparison purposes, the aftertreatment is carried out only with ammonia or with ammonia and a fabric softener, followed by a rinsing procedure.



TABLE 2

	perspiration alkaline			washfastness			fastness to rubbing	
	change in shade	staining		change in shade	staining		dry	wet
		wool	cotton		wool	cotton		
aftertreated according to DAS 1099494 (only ammonia)	4-5	5	4-5	4-5	5	5	5	2
aftertreated with ammonia and fabric softener	5	5	4-5	4	5	5	4-5	2
aftertreated according to the invention	5	5	5	5	5	5	5	4

A marked improvement in the fastness to rubbing (wet) can be achieved with the aftertreatment process of the present invention. In addition, the results of the washfastness and fastness to perspiration properties show that optimum fastness properties of the dyeings can also be obtained without the very wasteful rinsing procedure necessary according to the prior art at the conclusion of the aftertreatment.

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#### Example 3.

400 g of wool slubbing (non-shrinkproofed) is dyed with 5% of the dye of formula (3) by dyeing procedure D in a hank dyeing machine and subsequently aftertreated as described in Example 1. In a second aftertreatment, a rinsing procedure is carried out after step a) (ammonia treatment) in an aqueous liquor at room temperature and then follow steps b) (liquor temperature: 60°C) to d). The liquor volume for the rinsing procedure corresponds to the volume of the dye liquor. The fastness properties indicated in Example 1 are tested, and the washfastness is determined in accordance with SNV 195819.

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TABLE 3

	perspiration alkaline			washfastness			fastness to rubbing	
	change in shade	staining		change in shade	staining		dry	wet
		wool	cotton		wool	cotton		
aftertreated (according to Example 1)	5	5	4-5	5	5	4-5	4-5	3-4
aftertreated (with rinsing procedure after step a))	5	5	5	5	5	5	4-5	4

The results show that the already good general fastness properties, especially the fastness to rubbing (wet), can be further improved with the rinsing procedure after step a) of the aftertreatment process.

#### 5 WHAT WE CLAIM IS:—

1. A process for aftertreating dyeings on natural nitrogen-containing fibrous material which have been obtained in an acid dyebath with reactive azo dyes that contain as reactive groups radicals of a carboxylic acid which contains at least one reactive halogen atom and/or a multiple carbon to carbon bond that is capable of addition to the nitrogen-containing fibrous material, vinylsulphone groups or groups which form vinylsulphone groups under the stated dyeing conditions, or the radical of an aromatic heterocyclic ring system with two ring heteroatoms of which at least one is nitrogen and at least one reactive halogen atom, which process comprises treating the dyed fibrous material in the exhausted aqueous dyebath, in a single bath, but stepwise in succession,
  - (a) at 70° to 80°C. in an aqueous liquor having a pH of 8 to 9,
  - (b) at 55° to 65°C. with a reducing agent and a pH of the liquor of 4.5 to 5.5,
  - (c) at 55° to 65°C. with an oxidant to remove reducing agents not reacted in step (b), and optionally
  - (d) at 30° to 40°C. with a fabric softener, and subsequently finishing it by draining and drying.
2. A process according to claim 1 which comprises aftertreating dyeings on wool.
3. A process according to claim 2 which comprises aftertreating dyeings on wool which has been given a shrinkproof finish.

4. A process according to claim 3 which comprises aftertreating dyeings on wool which has been given a shrinkproof finish by oxidative processes and/or by applying synthetic resin.

5. A process according to claim 1, wherein the pH of the liquor is adjusted to 8 to 9 in step (a) with an inorganic or organic base.

6. A process according to claim 5, wherein the pH of the liquor is adjusted to 8 to 9 in step (a) with ammonia, alkali carbonates or bicarbonates or alkali ortho- or polyphosphates.

7. A process according to claim 5, wherein the pH of the liquor is adjusted to 8 to 9 in step (a) with a nitrogen-containing organic base.

8. A process according to claim 7, wherein an alkylamine or an alkanolamine is used as the base.

9. A process according to claim 1, in which the pH of the liquor is adjusted to 4.5 to 5.5 in step (b) with a low molecular organic carboxylic acid containing 1 to 4 carbon atoms.

10. A process according to claim 9, wherein the pH of the liquor is adjusted to 4.5 to 5.5 in step (b) with formic or acetic acid.

11. A process according to claim 1, wherein an alkali metal dithionite is used as reducing agent in step (b).

12. A process according to claim 1, wherein hydrogen peroxide is used as oxidant in step (c).

13. A process according to claim 1, wherein any one of oil, fat and wax emulsions, fatty acid condensation products, polyethylene, polyethylene glycol, siloxane and silicone oil emulsions, or a mixture thereof, is used as fabric softeners in step (d).

14. A process according to claim 13, wherein a mixture of polyethylene partially oxidised to contain carboxyl groups and a condensation product of dimerised fatty acids which are derived from unsaturated fatty acids containing 16 to 22 carbon atoms, and a polyalkylenepolyamine together optionally with paraffin and/or silicone oil, is used as fabric softeners in step (d).

15. A process according to claim 13 in which there is used as fabric softener a fatty acid/polyalkylenepolyamine condensation product, or the ammonium salt thereof, which is derived from fatty acids containing 16 to 22 carbon atoms.

16. A process according to claim 13 in which there is used as fabric softener a condensation product of dimerised linoleic or linolenic acid and diethylenetriamine or triethylenetetramine.

17. A process according to claim 13, wherein a mixture of 50 to 80 parts by weight of a polyethylene which contains carboxyl groups introduced by partial oxidation and 20 to 50 parts by weight of a condensation product of dimerised fatty acids and diethylenetriamine is used as fabric softener in step (d).

18. A process according to claim 17, wherein a mixture of 50 to 80 parts of a polyethylene which contains carboxyl groups, introduced by partial oxidation, 10 to 30 parts by weight of paraffin of m.p. 50—75°C. and 10 to 20 parts by weight of a condensation product of dimerised unsaturated fatty acids and diethylenetriamine is used as fabric softener in step (d).

19. A process according to any preceding claim, wherein the duration of the aftertreatment of the dyed fibrous material is 10 to 20 minutes in each of the steps (a) to (d).

20. A process according to any preceding claim, wherein the fibrous material is subjected to a rinsing procedure after step (a) in an aqueous liquor at room temperature and then further treated according to steps (b), (c) and, optionally (d).

21. A process according to claim 1, substantially as herein described.

22. The dyeings on natural, nitrogen-containing fibrous material after-treated by the process according to any preceding claim.

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